

# Parametrization of coarse grained force fields for dynamic property of ethylene glycol oligomers/water binary mixtures

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## Abstract

To evaluate shear viscosity of ethylene glycol oligomers (EGO)/water binary mixture by means of coarse-grained molecular dynamics (CG-MD) simulations, we proposed the self-diffusion-coefficient-based parameterization of non-bonded interactions among CG particles. Our parameterization procedure consists of three steps: 1) determination of bonded potentials, 2) scaling for time and solvent diffusivity, and 3) optimization of Lennard-Jones parameters to reproduce experimental self-diffusion coefficient and density data. With the determined parameters and the scaling relations, we evaluated shear viscosities of aqueous solutions of EGOs with various molecular weights and concentrations. Our simulation results are in close agreement with the experimental data. The largest simulation in this article corresponds to a 1.2  $\mu$ s atomistic simulation for 100,000 atoms. Our CG model with the parameterization scheme for CG particles may be useful to study the dynamic properties of a liquid which contains relatively low molecular weight polymers or oligomers.

**Keywords:** Coarse-grained molecular dynamics simulation, Ethylene glycol oligomer, Self-diffusion coefficient, Shear viscosity

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## 1. Introduction

Aqueous polymer solutions are widely used in industrial and household applications. For example, in ink-jet printing, polymer additives are used to control fixity and osmosis of the ink droplets to the paper. In order to estimate such properties, it is very important to understand the shear viscosity and the diffusivity of the polymer solutions. The molecular dynamics (MD) method at atomic level is the most common technique to estimate the shear viscosity of a solution or the self-diffusion coefficient of a component [1, 2]. However, even if a small oligomer of which the number of monomers is around 10, the longest relaxation time (for usual polymer solutions, it will be the rotational relaxation time of polymer chains), is several tens nanoseconds, which is about 1000 times longer than the characteristic time of water molecules. The rotational relaxation time of the polymer chains increases in proportion to some power of its molecular weight.

To obtain the ensemble averaged quantities, the sampling time (the time-average period) should be longer than the longest relaxation time of the system. The extreme long relaxation time complicates the estimations of the shear viscosity and the self-diffusion coefficient by using all-atom molecular dynamics (AA-MD) of which typical time-steps is femto-second order.

In order to extend the accessible time scale, the coarse-grained (CG) techniques have been developed for several decades. The CG techniques, in which some atomic groups are represented by a single particle, are widely used for simulations of meso-scale phenomena in soft materials (lipids, surfactants and polymers), for example, vesicle formation and fusion [3, 4], self-assembly [5, 6], micelle formation [7, 8, 9, 10] and pore formation in lipid bilayer [11, 12, 13, 14]. The coarse grained molecular dynamics (CG-MD) can achieve speed-up of up to several orders of magnitude faster than an AA-MD. Of course, the degree of speed-up depends on the details of the CG model or the system size. CG-MD method is very powerful tool to study of the static property, such as equilibrium structure of a large system, and it is also successful in investigating the fundamental mechanism of the long time-scale behaviors of soft materials.

To apply this method to a quantitative estimation of the dynamics, it should be noted that the time in CG-MD trajectory is not equivalent to the time in the all-atom (AA) description, due to the lack of atomistic details in the CG model. An effective method to obtain the consistency of the molecular motions between AA-MD and CG-MD is to multiply the time scale of

the CG-MD by a constant factor.

Recently, several authors reported the systematic studies of the dynamical and rheological properties of polymer systems (polystyrene melt [15, 16], polyamide-6,6 melt [16] and aqueous polyethylene glycol solutions [17]) by the multiscale approach that combines AA-MD and CG-MD simulations through the scaling of time in the CG model. With the well-tuned potential energy function among the particles in the CG model, CG-MD gives us the reasonable possibility to investigate both statical and dynamical properties of large scale systems which include macromolecules. However, there are few studies about the parametrization for the non-bonded CG interactions, which can be adapted to the estimations of dynamic properties of system, especially of the multi-component system.

In this article, we will present the results of the CG-MD simulations, including the systematic determination of the non-bonded parameters for the ethylene glycol oligomer (EGO)/water binary mixtures based on the self-diffusion coefficient and density data. We will also present the results of the shear viscosity of the mixture estimated by means of the nonequilibrium CG-MD simulations with the newly determined force field parameters. The article is organized as follows. The experimental methods for measurement of the shear viscosity and self-diffusion coefficient are explained in the section two. The explanation of the CG model and the force-field parametrization for EGO/water binary mixtures and the computational details are in the 3rd section. The results of the comparison between our simulations and the experimental measurements are shown in the Results and discussion section that follows.

## 2. Experimental section

### *2.1. Measurement of the shear viscosity and the self-diffusion coefficient*

#### *2.1.1. Materials*

Reagent grade diethylene glycol (DEG), tetraethylene glycol (TEG) and PEG600 were purchased from Sigma Aldrich Chemical Company and used in this work without further purification. EGO/water binary mixtures were prepared gravimetrically using distilled water. D<sub>2</sub>O with a minimum deuteration degree of 99.95 % (Merck Co. & Inc., Darmstadt, Germany) was used for all experiments as the NMR lock solvent.

### 2.1.2. Experimental details

The shear viscosities of the EGO aqueous solutions were measured at 293 K by the RE80 viscometer manufactured by Toki Sangyo Co., Ltd.

The self-diffusion coefficient measurements were performed at 293 K by pulse field gradient spin echo (PGSE)[18] using standard *ledbpgp2s* sequence on the Avance600 NMR spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany). To avoid mixing H<sub>2</sub>O in the aqueous EGO solution and D<sub>2</sub>O as the NMR lock solvent, we used NMR tubes which have a double tube structure. In the NMR tube, the inner tube was filled with the NMR lock solvent D<sub>2</sub>O, and the outer tube was filled with aqueous EGO solution.

In <sup>1</sup>H-NMR spectra of aqueous EGO solutions, the peaks of around  $\delta \approx 3.6$  ppm are assigned to the protons of CH<sub>2</sub>CH<sub>2</sub>O groups of EGO, and the peaks of around  $\delta \approx 4.7$  ppm are assigned to the protons of water molecule. The self-diffusion coefficients of assigned peaks are abbreviated in this article as  $D_{\text{EGO}}$  ( $\delta \approx 3.6$  ppm) and  $D_{\text{OH}}$  ( $\delta \approx 4.7$  ppm). Due to the proton exchange between hydroxyl groups of EGO end and water molecules, the diffusivity of EGO have a strong influence on the  $D_{\text{OH}}$ .

Under the assumption that the proton exchange between hydroxyl of EGO end and water molecules is very rapid, a self-diffusion coefficient of water ( $D_{\text{w}}$ ) can be obtained by [19]

$$D_{\text{w}} = \frac{\chi_i}{1 - \chi_i} D_{\text{OH}} - \frac{1}{1 - \chi_i} D_{\text{EGO}}, \quad (1)$$

where  $\chi_i$  is the molar fraction of hydroxylic protons of EGO ends, and  $D_{\text{w}}$  is the self-diffusion coefficient of water molecule.

## 3. Theoretical section

### 3.1. Coarse-graining of ethylene glycol oligomer and water

In our coarse-grained model, EGO molecules and water molecules are represented by coarse-grained particles, as shown in Figure 1.

EGO molecules are modeled by two types of particles ("PA") and ("PB"). The PA particle represents the oxyethylene unit of both ends of a ethylene glycol chain, and the PB particle represents the oxyethylene unit in a ethylene glycol chain. The mass of PA and PB particles are 53 amu and 44 amu respectively. A mass of an oxygen atom of ether is distributed to two adjoined coarse grained particles at an equal ratio.

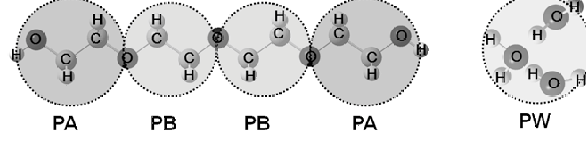


Figure 1: Coarse-graining scheme of a tetraethylene glycol and water. Water is modeled as a PW particle which corresponds to three water molecules.

Water is modeled by a single particle ("PW") corresponding to three real water molecules. The mass of PW particle is 54 amu. DEG, TEG and PEG600 molecules are modeled as PA-PA, PA-(PB)<sub>2</sub>-PA and PA-(PB)<sub>11</sub>-PA, and we expressed these EGO species as EGO2, EGO4 and EGO13 respectively.

### 3.2. Coarse-grained pair potential

We assume that the total potential energy for CG molecule is written as

$$U_{\text{tot}} = \sum U_{\text{b}}(L_{ij}) + \sum U_{\text{ang}}(\Theta_{ijk}) + \sum U_{\text{non}}(R_{ij}), \quad (2)$$

where the terms,  $U_{\text{b}}$ ,  $U_{\text{ang}}$ ,  $U_{\text{non}}$  are the effective potential functions of bond length  $L_{ij}$ , bond angle  $\Theta_{ijk}$ , and the distance between non-bonded CG particles  $R_{ij}$  respectively. Here,  $i$ ,  $j$  and  $k$  are the indices of the CG particles. The non-bonded CG interactions  $U_{\text{non}}(R_{ij})$  are modeled using the 12-6 Lenard-Jones potential,

$$U_{\text{non}}(R_{ij}) = 4\epsilon_{ij} \left( \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{R_{ij}} \right)^6 \right), \quad (3)$$

where  $\sigma_{ij}$  is the (finite) distance at which the inter-particle potential is zero,  $\epsilon_{ij}$  is the depth of the potential well. We use the Lorentz-Berthelot combination rule for interaction between the different species,

$$\epsilon_{ij} = \sqrt{\epsilon_i \cdot \epsilon_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}. \quad (4)$$

In the case the interaction between PB and PW particles,  $\epsilon_{ij}$  is calculated from the eq.(5) instead of eq.(4),

$$\epsilon_{ij} = \gamma \cdot \sqrt{\epsilon_i \cdot \epsilon_j}. \quad (5)$$

### 3.3. Scaling relations

As mentioned in Introduction, whenever the CG model is used, due to the lack of atomistic details, the speed of the time-evolution of the CG-MD trajectory is inconsistent with that of the AA-MD trajectory. To estimate of dynamical properties of the aqueous EGO solutions by means of CG-MD, we introduced the time mapping parameter  $S$ , which is defined by Kremer et.al.[15] as a ratio between the effective segment frictions in the AA model and in the CG model,

$$S \equiv \frac{\zeta^{\text{AA}}}{\zeta^{\text{CG}}}, \quad (6)$$

where  $\zeta^{\text{AA}}$  is an effective scalar friction coefficient of a segment in the AA model, and as  $\zeta^{\text{CG}}$  is ones in the CG model. In this article, we have assumed that the ratio between the shear viscosities in the AA model  $\eta^{\text{AA}}$  and in the CG model  $\eta^{\text{CG}}$  is equal to the parameter  $S$ , namely:

$$\eta^{\text{AA}} = S \cdot \eta^{\text{CG}}. \quad (7)$$

According to the Stokes-Einstein relation, the self-diffusion coefficient  $D$  is inversely proportional to  $\eta$  and the hydrodynamic radius of a segment  $r_h$ ,

$$D \propto (\eta \cdot r_h)^{-1}. \quad (8)$$

In our CG model, three water molecules are included in a single PW particle. The PW particle in the CG model has a larger hydrodynamic radius than the individual realistic water molecule, and thus the self-diffusion coefficient of water molecule in CG model is somewhat smaller than that in the AA model, even if we apply the time mapping parameter  $S$  properly.

We define the hydrodynamic radius  $r_h^{\text{CG}}$  of the molecule in CG model by

$$r_h^{\text{CG}} = \sqrt[3]{n} \cdot r_h^{\text{AA}}, \quad (9)$$

where  $n$  is a number of atomistic molecules, which are included in one coarse-grained molecule,  $n = 1$  (for EGO),  $n = 3$  (for water) as shown in Figure 1, and  $r_h^{\text{AA}}$  is the hydrodynamic radius of molecule in the AA model, the factor  $\sqrt[3]{n}$  in eq.(9) comes from the assumption of the linear relationship between the cube of the hydrodynamic radius of a molecule and its volume. From eqs.(7) and (8), the scaling relation between self-diffusion coefficients of molecular systems, which are described by the AA model and by the CG model, is given by

$$D^{\text{AA}} = S^{-1} \cdot \sqrt[3]{n} \cdot D^{\text{CG}}, \quad (10)$$

where  $D^{\text{CG}}$  is defined using the Einstein relation,

$$D^{\text{CG}} = \lim_{t \rightarrow \infty} \frac{1}{6t} \left\langle (r_{\text{com}}^{\text{CG}}(t) - r_{\text{com}}^{\text{CG}}(0))^2 \right\rangle, \quad (11)$$

where  $r_{\text{com}}^{\text{CG}}(t)$  is coordinates vector of the center of mass of the molecule in CG model at time  $t$ ,  $\langle \dots \rangle$  denotes the ensemble average. In this article,  $S$  is dealt with as a constant value for simplification, though the large molecular weight dependence of  $S$  is argued in the CG-MD study of polystyrene melt in Ref.15.

In order to determine  $S$ , we consider the self-diffusion coefficient of pure water using CG-MD simulation  $D_{\text{water}}^{\text{CG}}$ , and the experimental value  $D_{\text{water}}^{\text{EXP}}$  observed by NMR measurement. From eq.(10),  $S$  is given by

$$S = \frac{\sqrt[3]{3} \cdot D_{\text{water}}^{\text{CG}}}{D_{\text{water}}^{\text{EXP}}}. \quad (12)$$

#### 3.4. Parameterization of bonded potentials of EGO chain

The Boltzmann inversion method is well-known as one of the techniques to evaluate effective mesoscale potential from atomistic simulation [20]. This technique enables us to determine the bonded intramolecular interaction especially. In this article,  $U_{\text{b}}(L_{ij})$  and  $U_{\text{ang}}(\Theta_{ijk})$  are determined by this method. In a thermal equilibrium system, we assume that an appearance probability  $P$  of a state vector of a system  $Q$ , obeys the Boltzmann distribution.

$$P(Q) \propto \exp(-\beta U(Q)), \quad (13)$$

where  $U(Q)$  is a certain effective potential energy as a function of  $Q$ , and  $\beta$  is  $1/k_{\text{B}}T$ .

Once  $P(Q)$  is obtained, a effective potential  $U(Q)$  can be straightforwardly determined from the inversion of eq.(13). In this article, we assumed that all of the bonded (stretching / bending) potentials in the EGO chain are approximately given by the same  $U$ , as we will show in eq.(15).

To obtain  $P(L_{ij})$  and  $P(\Theta_{ijk})$ , the AA-MD simulation of a triethylene glycol dimethyl ether (TEGDE) in gas-phase is performed at 293 K. With our coarse-graining manner, a TEGDE molecule is modeled by three coarse-grained particles ( $\text{PB}_p, p = 1, 2, 3$ ) as shown in Figure 2.

The center of PB particle is defined as the center of mass of the oxyethylene monomer unit, in which two oxygen atoms at both ends of the unit are

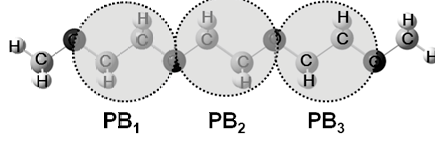


Figure 2: Coarse-graining scheme of a triethylene glycol dimethyl ether molecule.

weighted by 0.5 and other atoms are weighted by 1.0. Histogram  $H(L_{ij})$  of bond length (bond  $PB_1 - PB_2$  and bond  $PB_2 - PB_3$ ) and histogram  $H(\Theta_{ijk})$  of bond angle (bond angle  $PB_1 - PB_2 - PB_3$ ) are obtained from the 50-ns trajectory of the atomistic molecular dynamics simulation. Then, these histograms are renormalized by

$$P(L_{ij}) \propto \frac{H(L_{ij})}{L_{ij}^2}, \quad P(\Theta_{ijk}) \propto \frac{H(\Theta_{ijk})}{\sin(\Theta_{ijk})}. \quad (14)$$

As a technical subject for the  $U(Q)$ , because there are a lot of noises in the potential energy function obtained by the Boltzmann inversion scheme, it should be smooth by some appropriate functions. We assumed that the probability distribution function  $P(Q)$  can be expressed by the linear combination of Gauss functions  $G_l$  [21]. Then the effective potential energy functions  $U(L_{ij})$  and  $U(\Theta_{ijk})$  are obtained by

$$\begin{aligned} U(Q)/k_B T &= -\ln(P(Q)) = -\ln\left(\sum_{l=1}^m G_l\right) + const. \\ &= -\ln \sum_{l=1}^m \frac{A_l}{\xi_l \sqrt{\pi/2}} \exp\left(-\frac{(Q - \mu_l)^2}{2\xi_l^2}\right) + const., \end{aligned} \quad (15)$$

where  $A_l$ ,  $\mu_l$  and  $\xi_l$  are total area, center position and width of the Gauss function  $G_l$  respectively, and  $m$  is the number of the Gauss functions for smoothing of  $P(Q)$ . In this article, we decided  $m = 3$  for the both potentials of bond length ( $Q = L_{ij}$ ) and bond angle ( $Q = \Theta_{ijk}$ ). The areas ( $A_l$ ), center coordinates ( $\mu_l$ ) and widths ( $\xi_l$ ) are determined by curve fitting of the calculated bond length / bond angle distribution data.



### 3.5. Parameterization of Non-bonded potentials

In our CG model for the EGO / water binary system, there are three different particles (PA, PB, PW), and 7 parameters for the non-bonded interaction  $U_{\text{non}}(R_{ij})$ , which are  $\epsilon_{\text{PW}}$ ,  $\epsilon_{\text{PA}}$ ,  $\epsilon_{\text{PB}}$ ,  $\sigma_{\text{PW}}$ ,  $\sigma_{\text{PA}}$ ,  $\sigma_{\text{PB}}$  and  $\gamma$ . These non-bonded parameters for the  $U_{\text{non}}(R_{ij})$  are determined based on the experimental data (the densities and the self-diffusion coefficients for several EGO / water binary systems). The parameterization procedure consists of the four steps listed below.

STEP 1 : The parameter  $\epsilon_{\text{PW}}$  as a function of parameter  $\sigma_{\text{PW}}$  is determined so as to reproduce the density of pure water at 293 K, which is 0.998 g/cm<sup>3</sup> [22]. In order to satisfy the experimental pure water density,  $\epsilon_{\text{PW}}$  is uniquely determined according to  $\sigma_{\text{PW}}$ . The self-diffusion coefficient of pure water  $D_{\text{water}}^{\text{CG}}$  is evaluated by CG-MD simulation with the fixed parameter values ( $\epsilon_{\text{PW}}$  and  $\sigma_{\text{PW}}$ ). The time mapping parameter  $S$  is calculated from eq.(12). STEP 2 : The parameter  $\epsilon_{\text{PA}}$  as a function of parameter  $\sigma_{\text{PA}}$  is determined so as to reproduce the density of pure diethylene glycol (EGO2) liquid at 293 K, which is 1.118 g/cm<sup>3</sup> [23]. With the parameters for the PW determined in STEP 1, unique  $\sigma_{\text{PA}}$  is obtained through minimizing of the error between the  $D^{\text{CG}}$  calculated by CG-MD and the  $D^{\text{AA}}$  observed by NMR of the components in the EGO2/water binary mixtures (EGO2 weight fraction : 0.2, 0.5 and 0.8).

STEP 3 : For determination of the parameter  $\epsilon_{\text{PB}}$ , we used the density of pure tetraethylene glycol (EGO4) liquid at 293 K, which is 1.125 g/cm<sup>3</sup> [23] and the self-diffusion coefficients of the components in the triethylene glycol (EGO3)/water binary mixtures (EGO3 weight fraction : 0.2, 0.5 and 0.8) observed by NMR. The EGO4 and EGO3 are modeled in this article as PA-PB-PB-PA and PA-PB-PA, respectively. With the parameters for the PW and the PA determined already in STEP 1 and STEP 2, the  $\sigma_{\text{PB}}$  can be obtained by the same process in STEP 2. At the first execution of STEP 3,  $\gamma$  of eq.(5) is setted to 1. After performing STEP 4,  $\gamma$  is revised to the optimized value.

STEP 4: In the case of the calculating of the interaction between PB and PW particle, the parameter  $\gamma$ , which adjust the miscibility of the EGO chain in water, should be determined. The  $\gamma$  is obtained through minimizing of the error between the  $D^{\text{CG}}$  calculated by CG-MD and the  $D^{\text{AA}}$  observed by NMR of the components in the PEG600 (EGO13)/water binary mixtures (EGO13 weight fraction : 0.2).

STEP 3 and 4 are sequentially repeated until the proper  $\sigma_{\text{PB}}$  and  $\gamma$  are obtained. In STEP 2, 3 and 4, the root means of square errors (RMSE) are evaluated by

$$RMSE = \sqrt{\frac{1}{M} \sum_{q=1}^M (\log D_q^{\text{EXP}} - \log D_q^{\text{AA}})^2}, \quad (16)$$

where  $M$  is the number of data,  $D_q^{\text{EXP}}$  is experimental self-diffusion coefficients,  $D_q^{\text{AA}}$  is calculated self-diffusion coefficients from eq.(10).

### 3.6. Simulation details

All simulations of this work are performed by GROMACS 4.0.5 [24]. In the atomistic molecular dynamics simulation of gas phase of TEGDE, the temperature is held at  $T = 293$  K by Langevin thermostat [25] with correlation time  $\tau = 1.0$  ps. The production time step for integration is  $\text{dt} = 1$  fs. And cutoff radius for LJ and Coulomb potentials is 1.4 nm. The general Amber force field (GAFF) [26] is used as the atomistic force fields for TEGDE molecule. Atomic charges of a TEGDE molecule are assigned by AM1-BCC [27] method. These force fields and atomic charges are generated by antechamber 1.4 [28, 26] and acpype 1.0 [29]. In the CG-MD simulations, to evaluate the density and the equilibrated liquid structure, 2 ns MD simulations are performed in the  $NpT$  ensemble. Nose-Hoover thermostat [30, 31, 32] is used at 293 K to control temperature of the system. Parrinello-Rahman barostat [33] is used at 1 atm to control pressure of the system. In the 2 ns MD simulation, the instantaneous densities are calculated from the last 1 ns trajectory every 1000 steps and then are averaged. Omitting the first 1 ns data of trajectory as relaxation time, the self-diffusion coefficient is calculated from 3 ns (for water, EGO2/water, EGO4/water binary mixture) or 30 ns (for EGO13/water binary mixture) MD simulation, which is performed at constant volume  $NVT$  ensemble, at the initial structure is the last record of the former 2 ns MD simulation.

Non-equilibrium molecular dynamics(NEMD) [34] simulation is applied for the calculation of the shear viscosity of aqueous EGO solution. In order to calculate the shear viscosity, 20 ns (for water, EGO2/water, EGO4/water binary mixture) or 200 ns (for EGO13/water binary mixture) MD simulation is performed. After dropped first 5 ns trajectory, the shear viscosity is calculated by analysis of NEMD trajectory.

There are 5 sets of MD/NEMD simulations with different initial structures and initial velocity profiles. The diffusion coefficients or the shear viscosities are calculated from each MD/NEMD simulations, and then are averaged. The cutoff radius  $R_{\text{cut}} = 1.4$  nm for non-bonded interaction among the coarse-grained particles and a production time step  $\text{dt} = 10$  fs for integration of Newton's equation are used as common conditions in all CG-MD simulations.

## 4. Results and discussion

### 4.1. Bonded interactions for PEG chain

Parameters ( $A_l$ ,  $\mu_l$  and  $\xi_l$ ) of eq.(15), which are determined from curve fitting of the data of  $U(L_{ij})$  and  $U(\Theta_{ijk})$  are summarized in Table 1 and Table 2, respectively.

Table 1: Parameters of bond length potential represented by eq.(15)

bond type	l	$A_l$	$\mu_l(\text{nm})$	$\xi_l(\text{nm})$
PA-PA,PA-PB and PB-PB	1	0.382	0.023	0.305
	2	0.229	0.020	0.338
	3	0.028	0.018	0.266

Table 2: Parameters of bond angle potential represented by eq.(15)

angle type	l	$A_l$	$\mu_l(^{\circ})$	$\xi_l(^{\circ})$
PA-PB-PB and PB-PB-PB	1	238.840	57.471	190.567
	2	45.375	24.819	123.986
	3	31.826	14.765	101.560

Figure 3 shows the comparison between the AA model and the CG model for the histograms of the length  $L_{ij}$  (a) and of the angle  $\Theta_{ijk}$  (b) of bonded PB particles of TEDME, as shown in Figure 2.

### 4.2. Non-bonded interactions

The Lennard-Jones parameters for PW, PA and PB particles, the parameter  $\gamma$  of eq.(5) and the time mapping parameter  $S$  are straightforwardly determined by using the procedures (STEP 1 to STEP 4) mentioned as section 3.5. In STEP 1, to satisfy the experimental liquid density of pure water

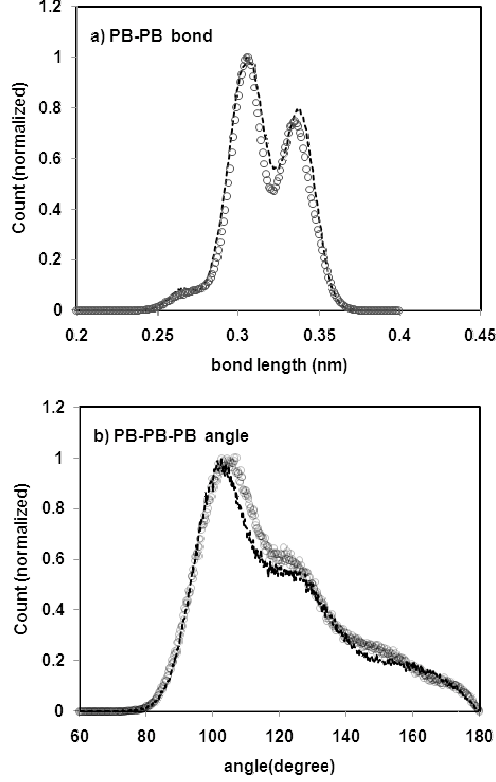


Figure 3: Probability distributions of bond length between bonded PB particles (a) and of bond angle among bonded PB<sub>1</sub>-PB<sub>2</sub>-PB<sub>3</sub> particles (b) of TEDME. Open Symbols denote the distribution obtained by using AA-MD simulation. Broken line denotes the distribution obtained by CG-MD simulation.

(0.998 g/cm<sup>3</sup>) at 293 K and 1 atm pressure,  $\epsilon_{PW}$  is uniquely determined according to  $\sigma_{PW}$ , which is limited in range from 0.38 to 0.42 nm. If the parameter  $\sigma_{PW}$  is within this range, then the PW fluid has a stable liquid phase. Though the  $\sigma_{PW}$  can be selected arbitrary within this range, we selected  $\sigma_{PW} = 0.40$  nm. The observed self-diffusion coefficient of pure water at 273 K and 1 atm pressure is  $D_{\text{water}}^{\text{EXP}} = 2.0 \text{ m}^2/\text{s}$  by using NMR. From eq.(12),  $S = 6.19$  is obtained from eq.(12). Through STEP 2 to STEP 4, the  $\sigma_{PA}$ ,  $\sigma_{PB}$  and  $\gamma$  parameters are one by one determined by minimizing the RMSE, which evaluated by eq.(16). These optimized non-bonded parameters are summarized in TABLE 3.

Table 3: Parameters of non-bonded potential represented by eqs.(3)-(5)

$\sigma_{PW}$	$\sigma_{PA}$	$\sigma_{PB}$	$\epsilon_{PW}$	$\epsilon_{PA}$	$\epsilon_{PB}$	$\gamma$
0.40	0.45	0.46	2.650	4.356	3.523	1.13

#### 4.3. Diffusion coefficients and shear viscosities of EGO/Water binary systems

From eq.(11), the self-diffusion coefficient is obtained by evaluating of the slope of the mean square displacement (MSD) of the center of mass of the EGO/water molecules. The MSDs were calculated for each EGO and water molecules in the simulation box using 3 ns (for water, aqueous EGO2 and EGO4 solutions) or 30 ns (for aqueous EGO13 solution) MD-simulation. Dropping the first 1 ns MSD data as relaxation time, the slope of MSD versus time was evaluated by linear regression.

Figure 4a and 4b show the comparison between experimental and calculated self-diffusion coefficients. Figure 4a shows the self-diffusion coefficients of the EGO molecules plotted against the EGO weight fraction ( $W$ ) of the EGO/water binary mixtures. Figure 4b shows the self-diffusion coefficients of the water molecules plotted in the same manner as Figure 4a. Three different EGOS, which are EGO2, EGO4 and EGO13, and three different EGO weight fractions ( $W = 0.2, 0.5$  and  $0.8$ ) are presented, including the data of aqueous EGO13 solutions ( $W = 0.5$  and  $0.8$ ), which did not used in the parametrization of non-bonded potentials at Section 4.2.

Experimental observations show that the self-diffusion coefficients (both of the EGO and the water) are linear on a log scale when plotted against  $W$ . The CG-MD simulation results are also linear as shown in Figure 4a and 4b. The dependence of the  $D$  on  $W$  is increasing against the EGO molecular weight ( $M_W$ ) as shown in Figure 4a, but the self-diffusion coefficients of the water molecule does not show such tendency (Figure 4b). The experimental  $W$  and  $M_W$ -dependences of  $D$  are reproduced by the CG-MD simulations correctly. Additionally, we performed CG-MD simulation of EGO45(PEG2000)/water binary mixture ( $W = 0.2$ ). We found that the calculated self-diffusion coefficients of EGO45 and water are comparable to the experimental values based on NMR [19] (data not shown), though these NMR measurements were observed at 298 K, differ from our CG-MD condition  $T = 293$  K.

The shear viscosity was calculated by the nonequilibrium method described

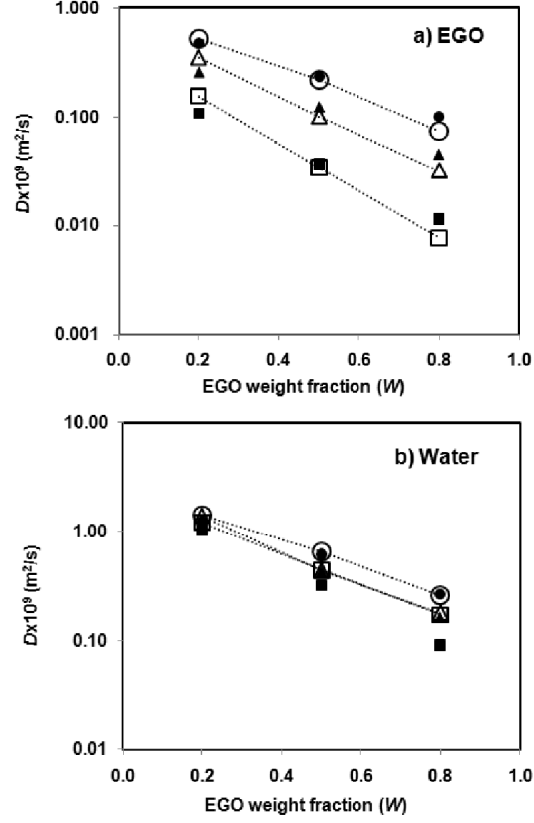


Figure 4: Self-diffusion coefficients  $D$  of EGO (a) and water (b) molecules as a function of the weight fraction  $W$  of EGO in the EGO/water binary mixtures. The open circles, the open triangles and the open squares denote the  $D^{\text{EXP}}$  values measured using NMR for EGO2/water, EGO4/water and EGO13/water binary mixtures, respectively. The filled circles, the filled triangles and filled squares denote the  $D^{\text{CG}}$  values calculated using CG-MD simulations for EGO2/water, EGO4/water and EGO13/water binary mixtures, respectively.

by B. Hess [34], which estimates the shear viscosity of liquid from nonequilibrium simulation with an external cosine acceleration profile of the form

$$\begin{aligned} a_x(z) &= A \cos(kz), \\ k &= \frac{2\pi}{l_z}, \end{aligned} \quad (17)$$

where  $a_x$  is the acceleration in the x direction,  $l_z$  is the height of the simulation box,  $A$  is the magnitude of acceleration,  $z$  is the coordinate z-direction. The

shear viscosity of liquid  $\eta$  can be estimated by

$$\eta^{-1}(t) = \frac{2k^2}{\rho A} \sum_{i=1}^N m_i v_{i,x}(t) \cos(kz_i(t)) / \sum_{i=1}^N m_i, \quad (18)$$

where  $\rho$  is the density of a system,  $m_i$  is the mass of the particle of index  $i$ ,  $v_{i,x}$  is the velocity in the x direction of the particle of index  $i$ ,  $N$  is the total number of particles in the simulation box,  $\eta^{-1}$  is the reciprocal of viscosity of the system. The  $A$  parameter must be carefully selected, the shear rate should not be so high that the system is driven too far from equilibrium. The maximum share rate of the CG system  $sh_{\max}^{\text{CG}}$  is

$$sh_{\max}^{\text{CG}} = A \frac{\rho}{\eta^{\text{CG}}} \frac{l_z}{2\pi}. \quad (19)$$

For our simulations with:  $\eta^{\text{CG}} \approx 0.01$  [ $kgm^{-1}s^{-1}$ ],  $l_z \approx 8$  [nm],  $\rho \approx 1000$  [ $kgm^{-3}$ ], and  $sh_{\max}^{\text{CG}}$  is approximately  $0.2$  [ $ps\ nm^{-1}$ ]  $A$ . This shear rate should be smaller than one over the longest correlation time in the system. For usually liquids, it will be the rotational correlation time of the largest molecule in the system. In the aqueous EGO13 solution ( $W = 0.8$ ), the rotational relaxation time of end-to-end vector of the coarse-grained EGO13 is approximately 6000 ps. In this case, parameter  $A$  should be smaller than  $0.001$  [ $nm\ ps^{-2}$ ]. When the shear rate is too high, the observed shear viscosity will be too low. In this article, we used  $A = 0.0005$  [ $nm\ ps^{-2}$ ] for all nonequilibrium CG-MD simulations.  $\eta^{\text{AA}}$  is estimated by eq.(9), with  $S = 6.19$  and  $\eta^{\text{CG}}$  obtained from eq.(18). Figure 5 shows the comparison between experimental and calculated shear viscosities of the aqueous EGO solutions. For nine EGO/water binary mixtures evaluated in this article, the symbols are same as in Fig.4, the calculated shear viscosities are agreed with the experiments. This means that the calculated values for two EGO-concentrations ( $W = 0.2$  and  $0.5$ ) are very close to the experimental data and overall data included  $W = 0.8$  shows the same tendency as the experimental results. In order to verify our CG model at larger molecular weight of EGO, we performed the additional calculations of the EGO22(PEG1000)/water and EGO45(PEG2000)/water binary mixtures. At the highest EGO-concentrations ( $W = 0.5$  for EGO22 and  $W = 0.4$  for EGO45) considered in this article, the rotational relaxation times of end-to-end vector of both the coarse-grained EGO22 and EGO45 are lower than the ones of the coarse-grained EGO13 in the aqueous EGO13

solution ( $W = 0.8$ ). Therefore, the parameter  $A$  in the eq.(18) and the sampling time length of  $\eta^{-1}$  are same as the case of the EGO13/water binary mixture ( $W = 0.8$ ). Figure 6 shows the comparison between our calculated results and the experimental observations measured at 293 K [35]. We found that the calculated viscosities are comparable to the literature values for aqueous EGO22 solutions. Although our calculated viscosities are slightly lower than the literature values for aqueous EGO45 solutions, the tendency of the dependence of viscosity on the EGO45 concentration seems to be in accordance with the experiments.

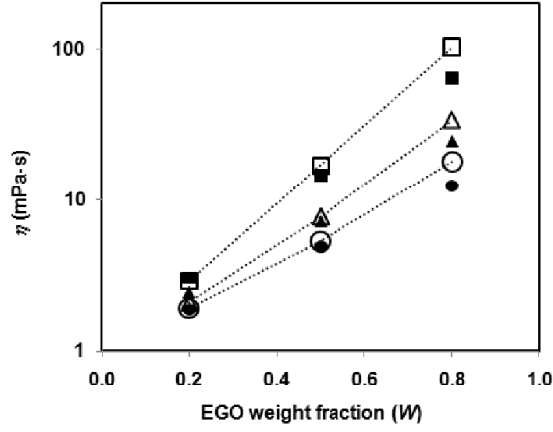


Figure 5: Shear viscosity  $\eta$  of the EGO and water binary mixture as a function of the EGO weight fraction  $W$ . The symbols are same as in Fig.4.



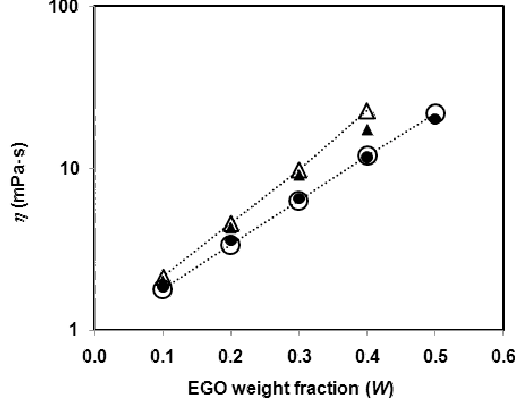


Figure 6: Shear viscosity  $\eta$  of the EGO and water binary mixture as a function of the EGO weight fraction  $W$ . The open circles and the open triangles denote the  $\eta^{\text{EXP}}$  values in literature [35] for EGO22(PEG1000)/water and EGO45(PEG2000)/water binary mixtures, respectively. The filled circles and filled triangles denote the  $\eta^{\text{CG}}$  values calculated using CG-MD simulations for EGO22/water and EGO45/water binary mixtures, respectively.

## 5. Conclusions

CG-MD simulations for the EGO/water binary mixtures were performed at 293 K and 1 atm pressure. The EGO chain was modeled by two types of particles, PA and PB, which represent the oxyethylene units of both ends and the middle of the chain, respectively. Also, three water molecules are included into a single PW particle. With our CG model, the number of particles that should be considered in the simulation can be reduced ten-fold, and the time step for integration of Newton's equation increases ten times compared with atomistic simulations.

The parameters for the CG model were determined by the systematic manner, as was shown in this article. The CG bonded potential parameters for the EGO chain were obtained by the Boltzmann inversion of the corresponding atomistic distribution functions. Due to the soft pair potential among the CG particles, the time-scale of CG-MD simulation is not equivalent to a realistic time scale. In order to estimate the proper dynamical properties by means of CG-MD simulations, the scaling relation for time in the CG model is introduced. Moreover, the hydrodynamic radius of PW particles in our CG model is larger than those of atomistic water molecules, due to the gain in volume of the PW particle as the result of the coarse graining of water,

as shown in Figure 1. Therefore, we also introduced the scaling relation for the water diffusivity based on the Stokes-Einstein law.

With the bonded potential parameters and the scaling relations, the 12-6 Lennard-Jones non-bonded potential parameters are straight-forwardly determined to reproduce the experimental observations (the density and the self-diffusion coefficient). We adopted the Lorentz-Berthelot mixing rule for the non-bonded interactions between the unlike particles. In this article, the Lorentz-Berthelot mixing rule is slightly modified, as shown in eq.(4) and eq.(5), to estimate the proper miscibility of the EGO13 in water. By using the determined CG force-field parameters for the EGO/water binary mixtures, our CG-MD simulation gives the estimations which agreed well with the experimental shear-viscosity data, including of the PEG1000/water and the PEG2000/water binary mixtures which were not used in our parameterization procedure. The largest simulation in this article corresponds to a 1.2  $\mu$ s atomistic simulation for 100,000 atoms. Our CG model with the parameterization scheme for the CG particles may be useful to study of the dynamic properties of a liquid which contains relatively low molecular weight polymers or oligomers.

In our future work, we plan to investigate the CG models for the several watersoluble polymers (e.g., polypropylene glycol, polyvinyl pyrrolidone, polyvinyl alcohol), for the estimations of the shear-viscosity and the diffusivity of these water mixtures through CG-MD simulations.

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